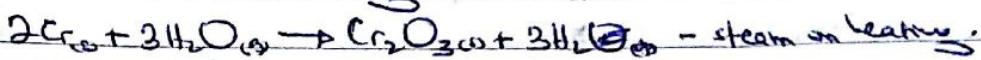
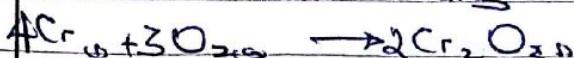


## Chromium: Reactions

(i) Steam at red heat heating \* No reaction with water



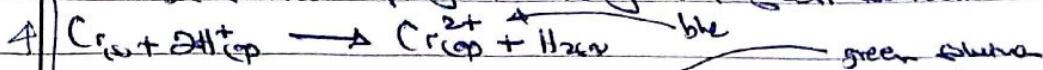
(ii) With air : carbon heating.



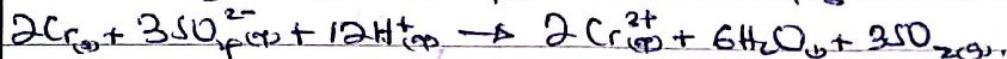
(iii) Reaction with acids

\* Non oxidising acids i.e HCl and dilute  $\text{H}_2\text{SO}_4$

- Form the solution rapidly oxidised by air to green colour.

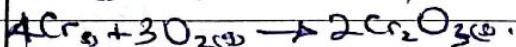
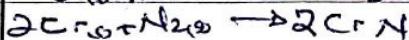


\* Oxidising acid:

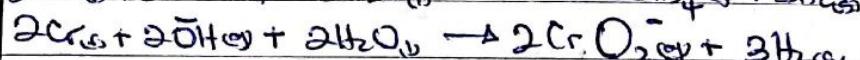
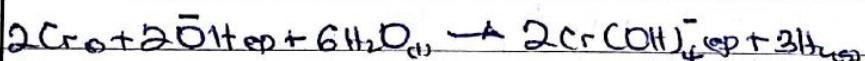


\* Nitric acid & Tannic chromium positive due to formation of thick oxide layer.

(iv) Non-metals

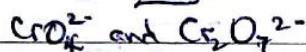


(v) With aqueous



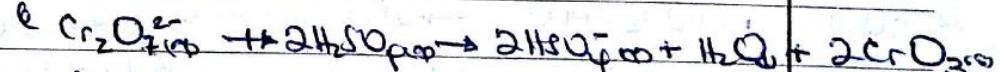
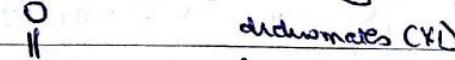
## Chromium (VI) Compounds

\* Oxidising:  $\text{Cr}^{6+}$  is highly oxidising. It exists as an oxo anion e.g.

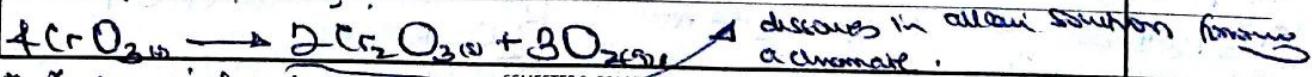


$\text{CrO}_3$  - red crystalline solid

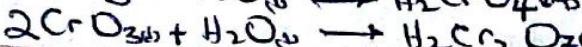
- Trigonal planar : formed by reacting conc  $\text{H}_2\text{SO}_4$  with chromate (IV) or



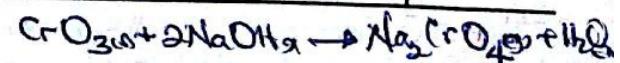
- decomposes on heating.



\* Anodic oxide dissolving in water



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Do not write in  
this margin

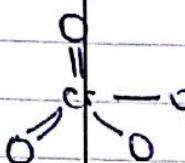
Write on both sides of the paper

Question.....

Chromates  $\text{CrO}_4^{2-}$  - yellow in colour, made by oxidising alkali chromate (IV) salts with sodium peroxide.

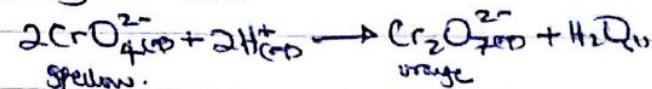


Shape:



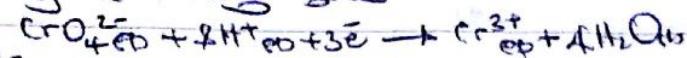
\* only exist in neutral or alkaline solution

\* in acidic solution, they turn into dichromate, orange in colour  
so they are basic

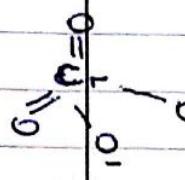


Tetrahedral:

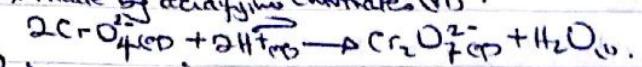
\* they are oxidising agents



Dichromates  $\text{Cr}_2\text{O}_7^{2-}$  - orange in colour.



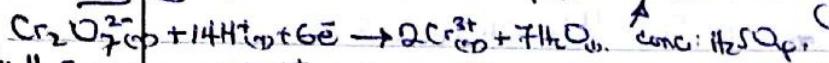
\* made by acidifying chromates (VI).



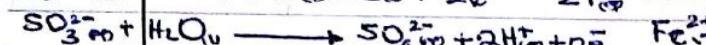
hexavalent anion



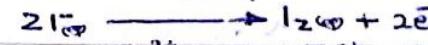
Oxidising agents:



$\text{H}_2\text{S}\text{ent}$



$2\text{I}^{\text{ep}}$



$\text{SO}_3^{2-}$



$\text{Fe}^{2+}$



Primary standard

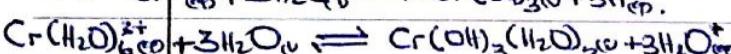
\* high molar mass;

\* stable on storage; \* if strong oxidising agent can be acidified by HCl.

Chromium III compounds (+3) & most stable

- Green due to existence of  $\text{Cr}(\text{H}_2\text{O})_6^{2+}$

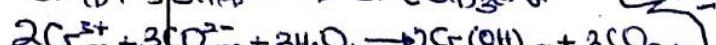
- Solution is acidic; because  $\text{Cr}^{2+}$  ions undergo hydrolysis forming hydrochromium ions which make the soln acidic.  $\text{Cr}^{2+}_{\text{ep}} + 3\text{H}_2\text{O}_{\text{ep}} \rightarrow \text{Cr}(\text{OH})_{3\text{ep}} + 3\text{H}^{\text{ep}}$ .



Chromium (III) hydroxide + green ppt.

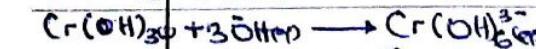


or  $\text{PPN}$



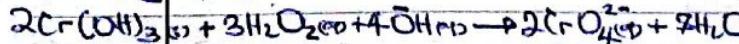
Amphoteric:  $\text{Cr}(\text{OH})_{3\text{ep}} + 3\text{H}^{\text{ep}} \rightarrow \text{Cr}^{2+}_{\text{ep}} + 3\text{H}_2\text{O}_{\text{ep}}$ .

conc. acidic



green soln.

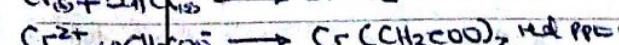
oxidised by  $\text{H}_2\text{O}_2$  in alkaline



Green

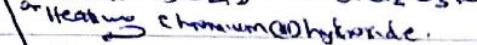
yellow

Chromium (II) compds & strong reducing agents



Chromium III oxide  $\text{Cr}_2\text{O}_3$  (green red)

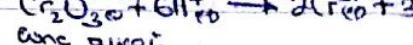
\* PPN: heating chromium in a stream of oxygen



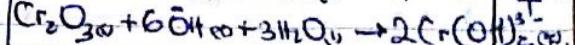
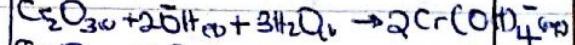
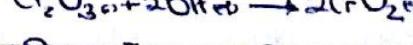
or Heating chromium(II) hydroxide.



Amphoteric

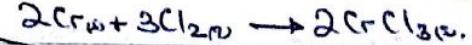


conc. acidic

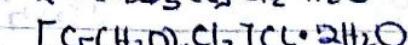
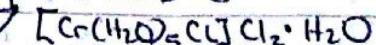
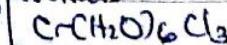


Chromium III chloride & green salt.

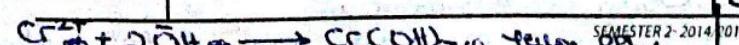
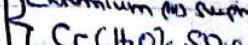
- Pass chlorine over heated chromium



exists as  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ ; has three isomers

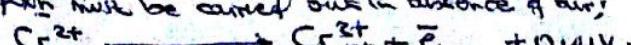


Chromium (II) sulphate + 6 $\text{H}_2\text{O}$  & chrysocolla



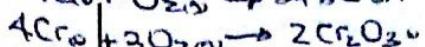
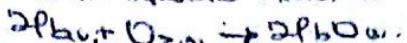
yellow ppt.

Precip must be carried out in absence of air

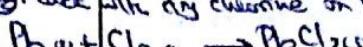


Simultaneous bim chemistry of chromium and lead:

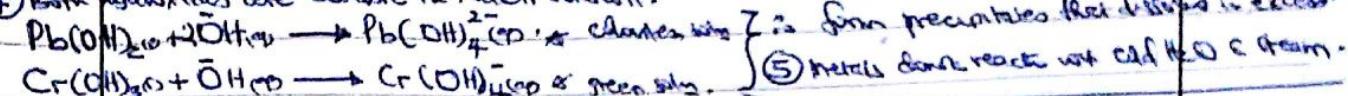
① Form amphoteric oxides on heating.



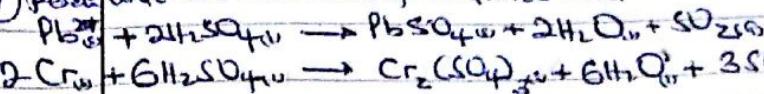
② React with dry chlorine on heating.



③ Both hydroxides are soluble in NaOH solution.



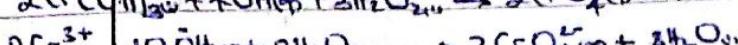
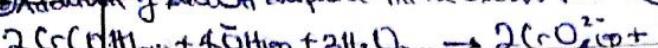
④ React with hot concentrated sulphuric acid.



Analysis of chromium (II) cation:

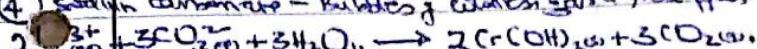
① Green ppt. soluble in excess NaOH.

② Addition of Al(OH) dispersion till in excess followed by H<sub>2</sub>O<sub>2</sub>.

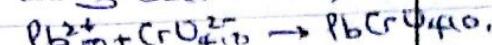


Yellow.

③ Sodium carbonate - bubbles of carbon dioxide & green ppt.

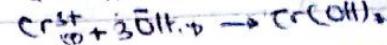


\* Formation of chromate can be confirmed by adding Lead(II) ethanolate; yellow ppt. formed.



④ Addition of NH<sub>3</sub>.

Green ppt. insoluble in excess.



yellow ppt.



### Examples:

1 (a) Write the electronic configuration of chromium

(b) State three characteristics of chromium as a transition metal.

(c) Chromium (II) chloride was dissolved in water and the solution tested with litmus. State what was observed and explain your answer.

(d) Ammonia solution was added dropwise to an aqueous solution of chromium (II) salt until excess.

(e) State what was observed.

(f) Write equation for the reaction.

(g) Explain the following observation.

When sodium hydroxide solution is added dropwise in excess to potassium chromium (II) sulphate solution, a green ppt. is formed that dissolves to form a deep green solution. On addition of H<sub>2</sub>O<sub>2</sub> the solution turns from green to yellowish brown.

(h) A dark purple crystalline solid Z, dissolves in water to give a violet solution. When excess dilute hydrochloric acid is added, dropwise until it excess, a green ppt. was formed until dissolved in excess to give a green solution.

(i) Identify the cation in Z.

(j) Write the formulae of the species responsible for the formation of

(k) violet solution.

(l) green solution.

(m) When H<sub>2</sub>O<sub>2</sub> was added to the green solution a yellow solution was formed when on treatment of ethanolic solution a yellow solid was formed.

(n) Write the equation for the reaction leading to the formation of (i) green solution (ii) yellow solid

(iii) yellow solution.

2 (a) Chromium is a transition element. State three properties of transition elements.

(b) Write electronic configuration of chromium.

(c) Using equations to illustrate why water, ethanol has chromium reacts with

(d) water

(e) dilute hydrochloric acid

(f) state what would be observed and write equation for the reaction that would take place when sodium sulphite is added to a solution of acidified potassium dichromate

(g)

(h) State three uses of chromium as a transition metal.

(i) State what would be observed and write equation for the reaction that would take place when sodium sulphite is added to an acidified solution of iron (II) sulphate.

(j)

(k) State three uses of chromium as a transition metal.

(l) State what was observed.

(m) Write the ionic equation for the reaction that took place.

(n) Write the chemical formulae of isomers of chromium (II) chloride, CrCl<sub>2</sub>. 6H<sub>2</sub>O

(o) State one way of distinguishing the isomers.

(P) Chromium (IV) sulphate was dissolved in water and after drops of concentrated sodium carbonate solution added to the solution.

(i) state what was observed

(ii) Give reason for your answer and write up to 5 words for this question.

b) Potassium chromate was dissolved in water, state the shape of the chromate ion.

c) To the solution in (b) was added a few drops of dilute sulphuric acid followed by excess sodium hydroxide droplets until in excess.

i) State what was observed

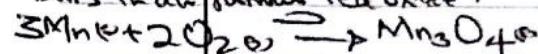
ii) Write equations for the reactions that took place.

Manganese  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$

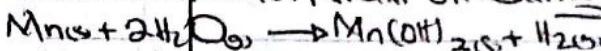
main o.e. +4; +7 and +2.

Reactions

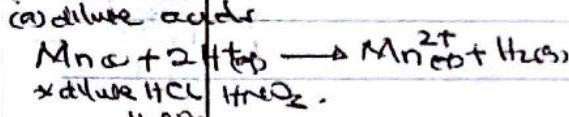
- Burns in air forming red oxide.



- React with bromates / chlorates on heating

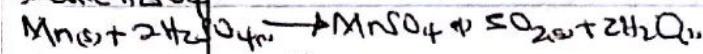


- With acids

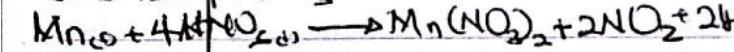


(b) concentrated acids

\* conc H<sub>2</sub>SO<sub>4</sub>

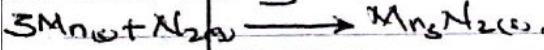


\* conc H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>

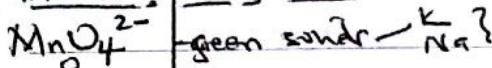


(c) With nonmetals (H<sub>2</sub>; C; Cl<sub>2</sub>; S)

- React on heating



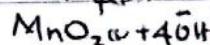
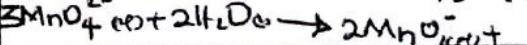
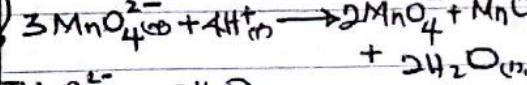
Manganese (VI) Compds



- The ion disproportionates in presence

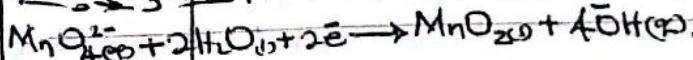
of an acid or H<sub>2</sub>O

$\begin{array}{c} 6 \\ | \\ O \\ || \\ \text{Mn} \\ | \\ O \end{array}$

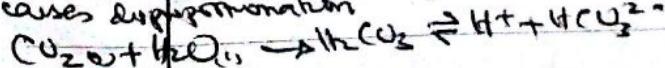


Green Solution turns to purple and a black brown solid.

Oxidising Property



∴  $MnO_4^{2-}$  only stable in alkaline solution, because disproportionates in neutral or acidic soln; even bubbling CO<sub>2</sub> through the solution causes disproportionation

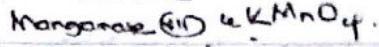
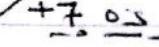
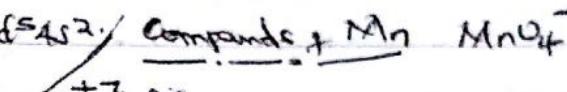
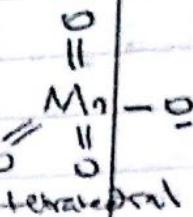


(B) State the common oxidation states of chromium and lead.

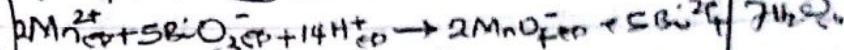
(b) Discuss the anomalies in the chemistry of chromium and lead. (Your answer should include Question)

(i) reactions leading to formation & complete

(ii) reactions with sodium hydroxide.



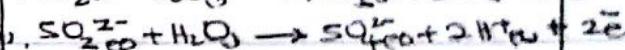
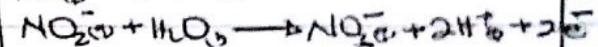
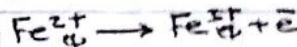
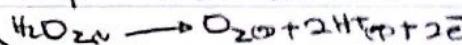
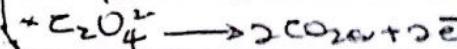
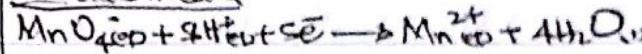
- powerful oxidising agent.



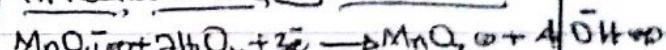
\* formed when Mn<sup>2+</sup> is oxidised by strong oxidising agents.

\* oxidising properties.

In acidic media

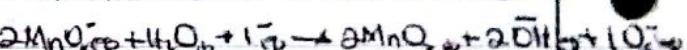


In neutral or slightly alkaline soln



\* weaker oxidising agent under these conditions.

- oxidises iodide to iodate in iodide.



Uses KMnO<sub>4</sub>

- volumetric analysis

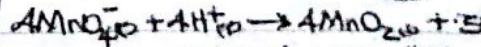
- titrimetric analysis of oxidisers,  $SO_2^{2-}$ ,  $ClO_4^-$

- oxidising agent in organic synthesis

Not a 1<sup>st</sup> standard

\* colour obtained in a high degree of purity from  $MnO_2$

\* deposits  $MnO_2$  on standing is unstable



\* cannot be purified by conc. HCl.



Add in dilute ammonia

- No indicator required

- oxidises amide range of soln

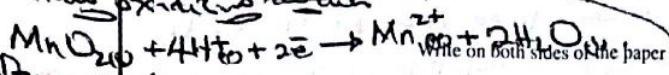
- fairly stable in  $H_2O$

- High relative molecular mass

## Manganese (IV) compound - $MnO_2$

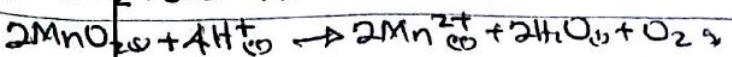
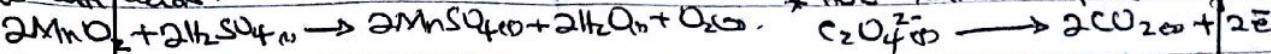
- Formed by heating  $Mn(OH)_2 \rightarrow MnO_{2(s)} + 2H_2O$ ,  $MnO_{2(s)} + 2OH^- \rightarrow MnO_4^{2-} + H_2O$ .

Strong oxidizing agent

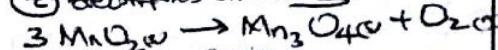


(Diamagnetic)

(i) with acids:



(ii) decomposes on heating

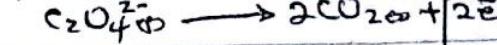


Question

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→ Oxidizing properties

\* Most oxalates in presence of conc  $H_2O_2$

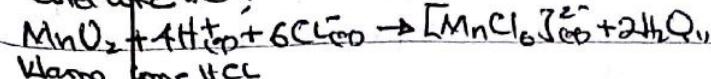


\* converts to chlorine on heating

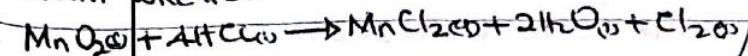


\* conc  $H_2O_2$  on heating.

- cord wire HCl;

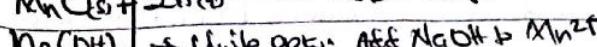
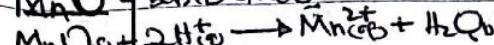


Warm conc HCl

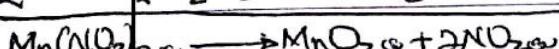
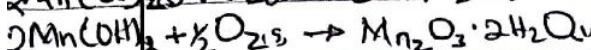
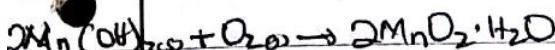


$Mn^{2+}$  CP's

$MnO$  - basic oxide:



$Mn^{2+} + 2OH^- \rightarrow Mn(OH)_2$  turns brown due to oxidation to brown solid



decomposition on heating

Analytical of  $Mn^{2+}$  iodide in excess

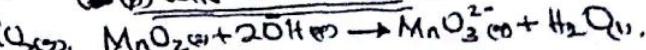
\*  $NaOH$  - white ppt turns brown on standing

\*  $NH_3$  → similar observations

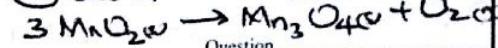
\* Add conc  $HNO_3$ ; followed by solid  $NaBiO_3$

$PbO_2$  and heat → purple soln formed.

(b) with caustic alkali



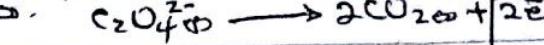
(c) decomposes on heating



Question

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this margin

\* most oxalates in presence of conc  $H_2O_2$



\* converts to chlorine on heating

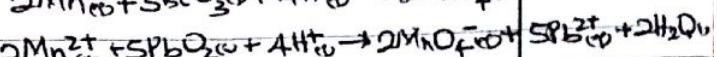
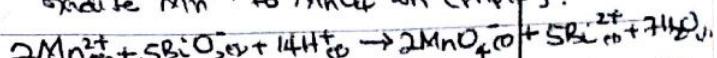


## Manganese (II) compounds

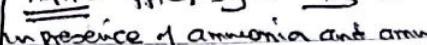
- most stable because of the presence of resonance

\* five singly occupied 3d-orbitals in the manganese (II) ion.

- strong oxidizing agents like lead(IV) oxide and sodium bisulfite in acidic condition oxidize  $Mn^{2+}$  to  $MnO_4^-$  ion (purple).



$MnS$  ppt'd by adding  $H_2S$  to a soln of  $Mn^{2+}$  in presence of ammonia and ammonium chloride the solubility prod of the sulphide is too high for it to ppt in acidic solution.

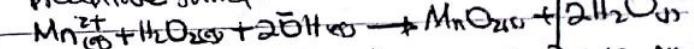


dissolves in dilute mineral acids



\* Addition  $H_2O_2$  in

- alkaline medium, filtered by  $H_2O_2$ ; dark brown/black precipitate formed.



\* addition of  $Na_2CO_3$  - white ppt formed:  $MnCO_3$ ;

$PbO_2$  and heat → purple soln formed.

## $MnF_6^{2-}$ ; $MnO_4^-$ ; $MnO_4^-$

Examples of complexes of  $Mn^{2+}$

\*  $Mn(H_2O)_6^{2+}$ ;  $Mn(CN)_6^{4-}$ ;  $Mn(CN)_6^{2-}$

### Example

(a) Explain what would be observed if aqueous sodium hydroxide solution was added to a solution containing manganese (II) ions drop wise until in excess.

(f) Name a reagent apart from aqueous ammonia and sodium hydroxide solution that can be used to distinguish manganese (II) ions from nickel (II) ions.

(i) state what would be observed if each of them is separately treated with the reagent you have named.

(4) Write the outer configuration of manganese

(i) State the possible oxidation states of manganese

(ii) How does the acidity of the oxides of manganese vary with increasing oxidation states.

(iii) What is the change in oxidation state of manganese when potassium manganate (IV) is reduced under alkaline conditions?

(iv) State four applications of potassium permanganate (IV) in laboratory exam.

oxidizing agent.

5(i) Iron(II) sulphate is normally used to standardise a solution of potassium manganate(VII). Acidified using sulphuric acid.

(ii) Write equation for the reaction between  $\text{KMnO}_4$  and  $\text{FeSO}_4$  sulphate. Do not write in this margin! Write on both sides of the paper.

(iii) State why hydrochloric acid is not used to acidity potassium manganate(VII) solution. Write on both sides of the paper.

(iv) A certain amount of acidified solution of potassium manganate(VII) reacted exactly with 25.0 mg of sodium nitrate. Calculate the concentration of sodium nitrate in moles per litre.

6 Potassium manganate(VII) is used as a  $\text{t}^{\circ}$  calibrant in volumetric analysis and has to be standardized.

(i) What is meant by a term "primary standard".

(ii) State three uses of  $\text{t}^{\circ}$  standard.

(iii) Explain why Potassium manganate(VII) is not used as a primary standard. Question

(iv) Name one substance Ethanolic silver nitrate that can be used as a primary standard for Potassium manganate(VII).

(v) Explain why hydrochloric acid is not ideally used to acidity solutions of potassium manganate(VII).

(vi) Acidified  $\text{KMnO}_4$  reacts with sodium nitrite.

(vii) Write half equations for the reaction.

(viii) The overall equation for the reaction.

(ix) 20.0 cm<sup>3</sup> of a 0.01 M manganese(VII) solution required exactly 16.65 cm<sup>3</sup> of solution

containing 8.8 g l<sup>-1</sup> of oxalate ( $\text{C}_2\text{O}_4^{2-}$ ) + 2H<sub>2</sub>O catalyse atomic mass of X.

Iron  $1s^2 2s^2 2p_6 3s^2 3p_6 3d^6 4s^2$   
common o's +2; +3:  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$   
oxides

iron pyrites  $\text{Fe}^{2+}$  Magnetite  $\text{Fe}_3\text{O}_4$   
& Haematite  $\text{Fe}_2\text{O}_3$  Limonite  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$   
 $\text{Fe}^{2+}$  spinel iron  $\text{FeCO}_3$ .

### Extraction

\* Blast furnace.

\* Iron ore + limestone + coke heated in blast furnace.

\* Hot air is passed thru to furnace from bottom

\* coke burns  $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$

\* coke reduces  $\text{CO}_2 \rightarrow \text{CO}$

\* CO and C.  $\rightarrow 2\text{CO}_2$

\* CO and  $\text{Fe}_2\text{O}_3$  reduces iron oxide

$\text{Fe}_2\text{O}_3 + 3\text{CO} \rightarrow 2\text{Fe} + 3\text{CO}_2$

\* Lime stone decomposes at  $1000^{\circ}\text{C}$

$\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$ ;  $\text{CaO}$

combines with impurities forms slag;

calum shale.

$\text{CaO} + \text{SiO}_2 \rightarrow \text{CaSiO}_3$

$\text{CaO} + \text{Al}_2\text{O}_3 \rightarrow \text{CaAl}_2\text{O}_4$ .

\* Molten iron sinks at bottom with  $\text{MnO}$

floats on top tapped off differently.

\* Molten iron =  $\text{Fe}_3\text{O}_4$  or  $\text{Fe}_2\text{O}_3$  iron = impure ( $\text{P}, \text{C}, \text{S}, \text{Si}$ )

\* Purified iron converted to steel.

### Chemical properties

(1) air  
in presence of moisture, it readily rusts forming a brown shade.

$2\text{Fe} + \frac{3}{2}\text{O}_2 + \text{XH}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3 \cdot \text{XH}_2\text{O}$

\* Not affected by dry air at room temperature.

\* Heated iron reacts with oxygen to form black solid  $\text{Fe}_3\text{O}_4$  and iron(III) oxide.

$3\text{Fe} + 2\text{O}_2 \rightarrow \text{Fe}_3\text{O}_4$

$4\text{Fe} + 3\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3$ .

(2)  $\text{H}_2\text{O}$

\* Pure iron doesn't react with pure cold water.

\* Heated iron reacts with water forming steam.

$3\text{Fe} + 4\text{H}_2\text{O(g)} \rightleftharpoons \text{Fe}_3\text{O}_4 + 4\text{H}_2\text{O}$ .

### With acids.

Non oxidising acidic dilute  $\text{HCl}$  & dilute  $\text{H}_2\text{SO}_4$ .  
 $\text{Fe} + 2\text{H}^{+} \rightarrow \text{Fe}^{2+} + \text{H}_2$  (because it is fairly electropositive iron) salt is obtained.

Oxidising acids:

Atmos  $\text{HNO}_3 \rightarrow$  iron(III) salt is formed.  
conc  $\text{HNO}_3 \rightarrow$  tends to retain positive charge to formation of  $\text{Fe}_3\text{O}_4$  on the metal.

conc  $\text{H}_2\text{SO}_4$  and heat  $\rightarrow$  iron(III) salt formed +  $\text{NO}_2$ .

$2\text{Fe} + 6\text{H}_2\text{O}_4 \rightarrow \text{Fe}_2(\text{O}_4)_3 + 6\text{H}_2\text{O}$ , + 3  $\text{NO}_2$ .

### With non-metals

Reacts with non-metals on heating

$\text{Fe} + \text{S} \rightarrow \text{FeS}$  (black solid)

$2\text{Fe} + \text{Cl}_2 \rightarrow 2\text{FeCl}_3$  (black sublimate).

### Compounds

+3 O's more acidic because has half-filled 3d orbital than +2 O's.

### O's +2 compounds

(1)  $\text{FeO} \rightarrow$  black sand.

$\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_{2-\delta} \text{O}_{3+\delta} + \text{CO}_2$ .

\* Readily oxidised over heated in air

$4\text{FeO} + \text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3$ .

\* Basic on the Mohr reaction with dilute acid

$\text{FeO} + 2\text{H}^{+} \rightarrow \text{Fe}^{2+} + \text{H}_2\text{O}$ .

\* Disproportionates when heated in air were atmosphere loss iron and  $\text{Fe}_3\text{O}_4$ .

$4\text{FeO} \rightarrow \text{Fe}_3 + \text{Fe}_3\text{O}_4$ .

### (2) Iron(II) hydroxide

- Green ppt found when aqueous  $\text{NaOH}$  or  $\text{NH}_3$  is added to a solution of iron(II) salt.

$\text{Fe}^{2+} + 2\text{OH}^{-} \rightarrow \text{Fe}(\text{OH})_{2-}$

\* Readily oxidised to brown iron(III) hydroxide when exposed to air

$4\text{Fe}(\text{OH})_2 + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{Fe}(\text{OH})_3$ .

\* Readily dissolves in dilute acids forming aqueous

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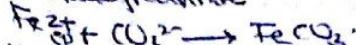
Ammonium:

$\text{Fe}(\text{OH})_2 + \text{H}^{+} \rightarrow \text{Fe}^{2+} + \text{H}_2\text{O}$ .

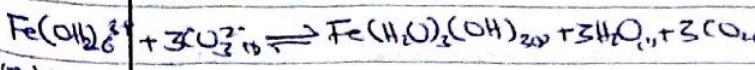
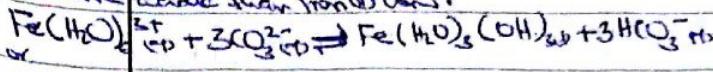
$\text{Fe}^{2+} + 6\text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{H}_2\text{O})_6^{2+}$ .

③ Iron(II) carbonate substrate.

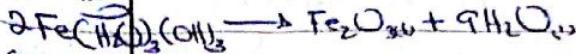
→ White precipitate



\* Must be formed from boiled water which haven't contact air because it oxidizes readily to  $Fe(OH)_3$ . Write on both sides of the paper if iron(III) carbonate doesn't exist because iron(II) ions are more acidic than iron(III) ions.



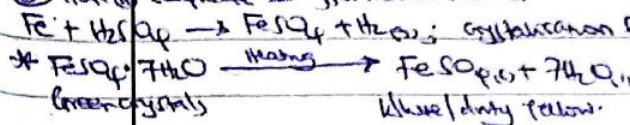
→ Leaves



④ Iron(II) sulphide → Black solid.



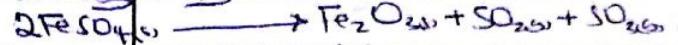
⑤ Iron(II) sulphate → Effervescent solid



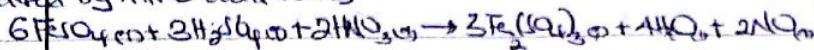
\*  $FeS_{(s)} + 7H_2O \xrightarrow{\text{heating}} FeSO_4 \cdot 7H_2O$

(green crystals) white/dirty yellow.

\* Shows heating



\* Reduced by nitric acid (conc)

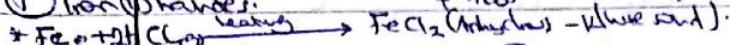


⑥ Iron(II) ammonium sulphate  $FeS_2(NH_4)_2SO_4 \cdot 6H_2O$

\* Not effervescent & stable in air so doesn't get oxidized

\* Used as a primary standard in titrations  $KMnO_4$  etc.

⑦ Iron(II) chlorides:



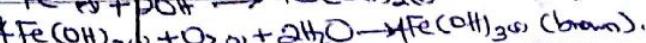
(white/grey solid)

\* Among clear Fe dioxides → metal greys iron(II) chlorides.

Theorectical chemistry of iron(II) ions

①  $NaOH$  (aq) and  $NH_3$  (aq).

→ Green ppt Irreversible in excess, turns brown on heating.

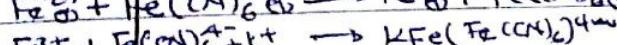


② Potassium hexacyanoferrate(II) solution

→ Blue ppt which turns reddish brown.

③ Potassium hexacyanoferrate(II) solution

→ Same blue ppt formed.



Blue ppt

④ Potassium thiocyanate

→ No observation but gives same character after due to aerial oxidation of  $Fe^{2+} \rightarrow Fe^{3+}$ .

⑤ Dimethylglyoxime solution (DMG)

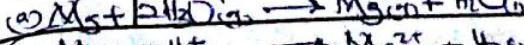
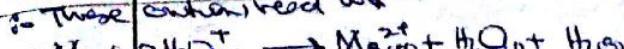
→ Shows red colour.

Iron(III) compounds

→ Solutions in water strongly acidic because iron(III) ions exist as  $Fe^{3+}$  in solution.  $Fe^{3+}$  has a small ionic radius, high charge & high polarizing power, undergoes hydrolysis in water forming hydronium ions in solution making the solution acidic.

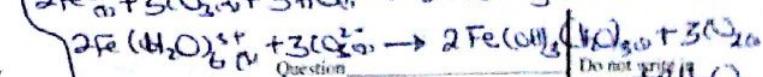


→ These cations react with



→ Releasing hydrogen gas.

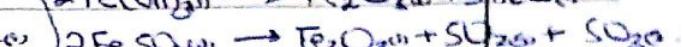
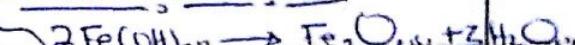
→ React with sodium hydroxide carbonate reaction forming brown ppt and bubbles of carbon dioxide.



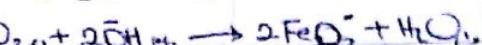
Question

Do not write this down

Iron(III) oxide  $Fe_2O_3$

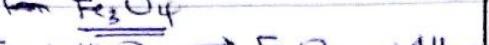


Amphoteric

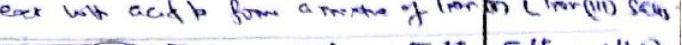


Reactions similar & similar to  $Al_2O_3$

Iron(III) oxyferrite



\* React with acid to form a mixture of iron(II) & iron(III) salts



Iron(III) hydroxide



Amphoteric



Heats



Iron(II) hydroxide  $\rightarrow 2Fe(s) + 3X_2(s)$

$FeCl_2$  &  $FeBr_2$   $\Rightarrow$  Corrosive smoke turns brownish in vapour phase

X



X can be readily hydrolysed in solution.

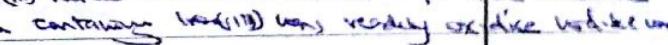


\* Iron(III) hydroxide cannot be obtained in pure form because colour containing iron(II) ions readily oxidise back to iron(III).

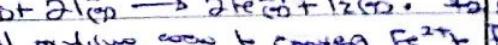


It is a very useful oxidising agent to convert  $Fe^{2+} \rightarrow Fe^{3+}$ .

$Fe_2(OH)_3$

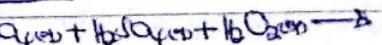


When heated



Aqueous chemistry of iron(III) ions

①  $NaOH$  and aqueous  $H_2O_2$   $\Rightarrow$  Brown ppt



② Potassium hexacyanoferrate(II) solution

\* Dark blue ppt

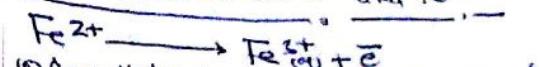
③ (III) solution  $\Rightarrow$  Brown coloration

SEMESTER 2-2014/2015

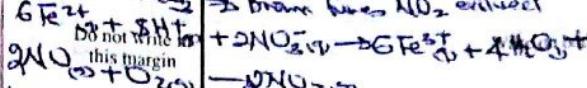
④ Potassium thiocyanate solution  $\Rightarrow$  Blood red solution.

Scanned by CamScanner

### Interconversion b/w $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$



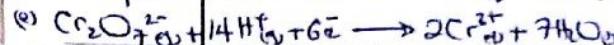
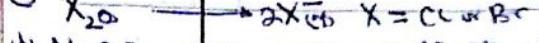
(i) Concentrated  $\text{HNO}_3$  → Brown fumes  $\text{NO}_2$  evolved



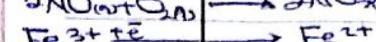
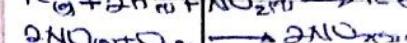
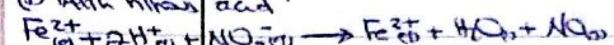
(ii)  $\text{MnO}_4^-$  (this margin) +  $\text{H}_2\text{O}_2$  →  $\text{Mn}^{2+}$  +  $2\text{H}_2\text{O}_2$



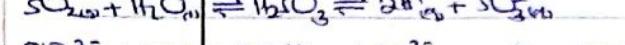
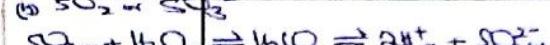
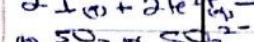
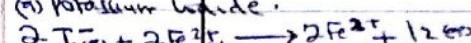
(iii)  $\text{H}_2\text{O}_2 + 2\text{H}^+$ ,  $\rightarrow 2\text{H}_2\text{O}_2 + 2e^-$



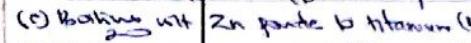
(d) With nitric acid.



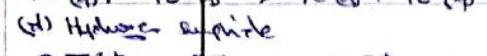
(e) Potassium iodide.



(c) Heating with Zinc powder to titanium (IV) chloride.



(f) Hydrogen sulphite



### Examples

### Cobalt $[\text{Ar}] 3d^7 4p^3 3d^7 4s^2$

Common oxidation states  $+2, +3$ .

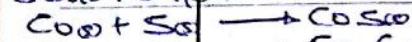
#### Reactions

\* Not affected by heat, air according to TGA.

\* It when reacts with oxygen to form cobalt(II) oxide and at high temperatures to form cobalt(III) oxide, i.e. cobalt tetroxide.



\* React with non-metals on heating



#### Reaction with acids

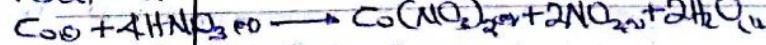
With  $\text{HCl}$  &  $\text{H}_2\text{SO}_4$  → Intermediate  $\text{H}_2\text{O}_2$  and

form a corresponding salt. But it is now.



concentrated acid renders the metal passive but

reacts with dilute nitric acid.



\* Cobalt doesn't react with alkalis.

#### Compounds of Cobalt

Stable o.f.  $+2$ .

$+3$  oxidation is highly oxidising readily reduced to

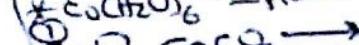
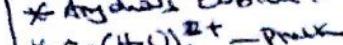
$+2$  at  $20^\circ\text{C}$ . But stable in presence of complexing

agents e.g.  $\text{NH}_3$ ,  $\text{CN}^-$  etc.

\*  $+3$  oxides water as  $\text{CO}$  cannot exist in water.

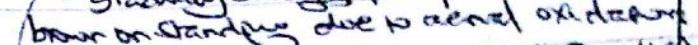
### Cobalt (II) complexes

\* Anywhere cobalt (II) exists like



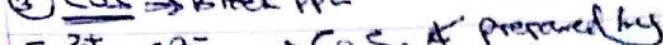
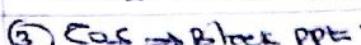
gradually changes pink/blue ppt.

brown on standing due to aerial oxidation.



Prone to hydrolysis.

dissolves readily in dilute acids forming pink solution

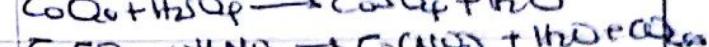


\* Prepared by passing  $\text{H}_2\text{S}$  through a  $\text{Co}(\text{II})$  salt in presence of aqueous ammonia and ammonium chloride.

\* Stability product of  $\text{CoS}$  is too large to be

soluble in acidic solution. In presence of  $\text{NH}_3/\text{NH}_4\text{Cl}$  buffer to hydrogen ions in

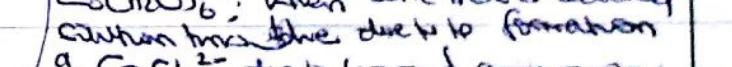
soln.



#### Addition of conc HCl

\* chloride  $\text{Co}^{2+}$  is pink due to presence of  $\text{Co}(\text{H}_2\text{O})_6^{2+}$ . When conc HCl is added

it turns brown due to formation of  $\text{CoCl}_4^{2-}$  due to ligand exchange.



Pink

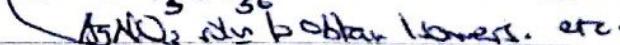
\* It becomes light on rise or increase in  $[\text{HCl}]$  and temperature (dries away water to steam).

#### Complexes

$\text{Co}(\text{II})$  complexes more stable than  $\text{Co}(\text{III})$  complexes. It's easily reduced to  $\text{Co}(\text{II})$  complexes except  $\text{Co}(\text{H}_2\text{O})_6^{2+}$ .

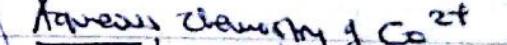
e.g.  $\text{CoCl}_3(\text{NH}_3)_6 \rightarrow$  Can be analysed using

$(\text{NH}_3)_6 \rightarrow$  obtain  $\text{Co}^{2+}$ , etc.



#### Aqueous chemistry of $\text{Co}^{2+}$

①  $\text{NaOH} \rightarrow$  blue ppt. insoluble in excess conc HCl with excess  $\text{NH}_3$



Pink/grey pink/brown ppt.



Pink/grey pink/brown ppt.



Pink/grey pink/brown ppt.



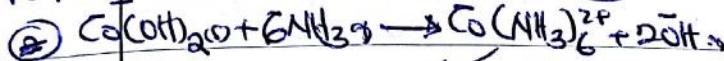
Pink/grey pink/brown ppt.



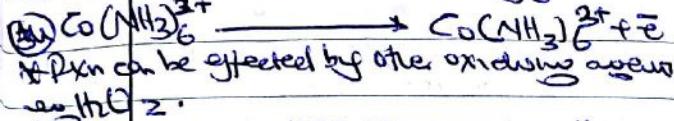
Pink/grey pink/brown ppt.

(2)  $\text{NH}_3$  soln: Blue ppt insoluble in excess and turns red on standing.  
 $\text{Co}^{2+} + 2\text{OH}^- \rightarrow \text{Co}(\text{OH})_2(s)$ .

conc: Blue ppt soluble in excess forming a red soln which turns yellowish brown on standing.



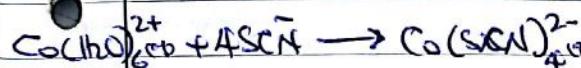
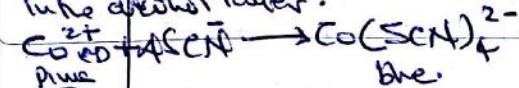
In air this oxidized to  $\text{Co}(\text{NH}_3)_6^{2+} \rightarrow$  yellow.



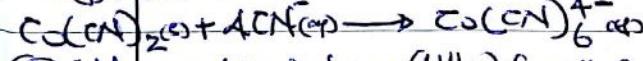
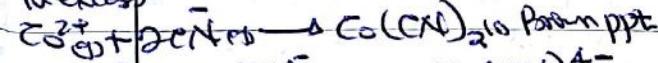
(3) Addition of conc HCl: Pink soln turns blue  
 $\text{Co}(\text{H}_2\text{O})_6^{2+} + 4\text{Cl}^{-} \rightarrow \text{CoCl}_4^{2-} + 6\text{H}_2\text{O}$ . On dilution blue solution turns back to pink.

(4) Potassium thiocyanate & Ammonium thiocyanate.

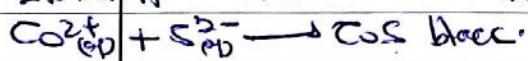
→ Blue solution formed which can be extracted in an alcohol → Blue soln occurs in the alcohol layer.



(5)  $\text{KCN}$  soln. → Reddish brown ppt soluble in excess.



(6) Addition of sulphide e.g.  $(\text{NH}_4)_2\text{S}$  or  $\text{H}_2\text{S}$  → Black ppt insoluble in dilute HCl.



Nickel  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9 4s^2$ .

$0s \rightarrow 2\text{d}(\text{sh}\text{b})$ ; +3 (rare).

\* Aqueous soln appear green due to  $\text{Ni}(\text{OH})_6^{2+}$  ions.

$\text{NiO}$  → green solid which is basic.  $\text{Invisible}$  in excess.

$\text{Ni}(\text{OH})_2$  → green solid formed when  $\text{Ni}(\text{OH})_6^{2+}$  added. soluble in ammonia forming a  $\text{Ni}^{2+}$  soln due to  $\text{Ni}(\text{H}_2\text{O})_6^{2+}(\text{NH}_3)_4^{2+}$  and  $\text{Ni}(\text{NH}_3)_6^{2+}$

Complexes of Ni

$\text{Ni}(\text{H}_2\text{O})_6^{2+}$  - green  $\text{Ni}(\text{NH}_3)_6^{2+}$  deep blue.

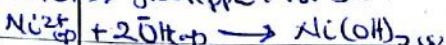
$\text{Ni}(\text{CN})_4^{2-}$  - orange  $\text{Ni}(\text{L})_4^{2-}$  like  $\text{Ni}(\text{O})_4^{2-}$

oxidation state of Ni is zero; Tetra carbonyl nickel(0). \* Methylmethylenebiquinoxime = Red ppt when SEMESTER 2-2014/2015

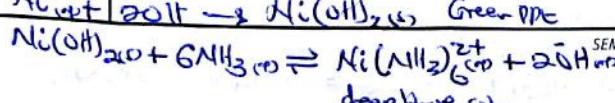
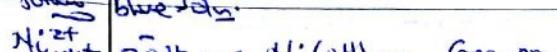
NH<sub>3</sub> is added to  $\text{Ni}^{2+}$  soln.

Aqueous chemistry

(1)  $\text{NaOH}$  → green ppt insoluble in excess



(2) Aqueous ammonia → green ppt soluble in excess forming blue soln.



(5)  $\text{AgNO}_3 \rightarrow$  Add dilute ammonia soln until in excess, followed by  $\text{AgNO}_3 \Rightarrow$  Red ppt.



(6) Sodium sodium carbonate solution.

Green ppt Question:  $\text{Ni}^{2+} + \text{CO}_3^{2-} \rightarrow \text{NiCO}_3$  do not write in this margin

(5) Ammonia sulphide → Black ppt formed.



(6) Potassium hexacyanoferrate (II) soln green ppt soluble in ammonia soln.

(7) Potassium hexacyanoferrate (II) soln Brown ppt.

(8) Potassium cyanide soln → yellow green ppt soluble in excess.

(9) 2 Naphthol → Brown ppt soluble in dilute HCl

Copper  $1s^2 2s^2 2p^6 3s^2 3p^2 3d^{10} 4s^1$ ; common oxidation states +1, +2

$\text{Cu}^{+} 1s^2 2s^2 2p^6 3s^2 3p^6 2d^1$  +1 very unstable and disproportionates to  $\text{Cu}^{2+} 1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$  copper +  $\text{Cu}^{+}$



Stability  $\text{Cu}^{2+}$

\*  $\text{Cu}^{2+}$  though with partially filled 3d orbital is more stable than  $\text{Cu}^{+}$  which has a fully filled 2d orbital. Since lone pair in compounds and aqueous solution then hydration and lattice energy have to be assessed.

\* Copper (II) ions have greater charge density than  $\text{Cu}^{+}$  and hence with stronger hydration energy compared to  $\text{Cu}^{+}$  have more stability in aqueous solutions forms hexaaqua copper (II) ions solution.

The extra energy required for second ionisation energy is compensated by the hydration energy so much that copper (II) ion loses an electron to become  $\text{Cu}^{+}$  which then releases the hydration energy.

\* Lattice energy is dependent on ionic charge and small ionic radius, these make copper(II) compounds more stable than copper(I) compounds.

Occurrence  $\leftarrow$   $\text{CuFeS}_2$  - copper pyrite + main ore.

$\text{Cu}_2\text{S}$  - copper glance

$\text{Cu}_2\text{O}$  - copper cuprite

$\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$  - malachite

Extraction

(1) Concentration by float flotation

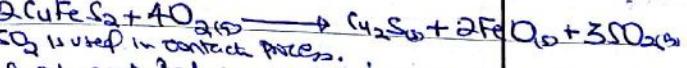
- mix ore with  $\text{H}_2\text{O}$  and pine oil

- Blow air into mixture to agitate it.

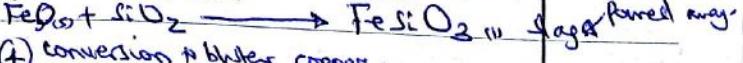
- copper containing particles collect in float bath and are skimmed off, filtered and dried.

(2) Flotation ore

- one floated in air - ion is oxidised to iron(II) oxide



(3) Stacking → product of roasting is heated in absent furnace with silica.



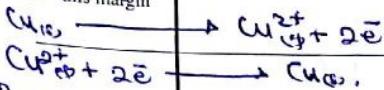
(4) conversion to blister copper.

-  $\text{Cu}_2\text{S}$  is heated in air forming  $\text{Cu}_2\text{O}$  which reacts with  $\text{Cu}_2\text{S}$  to form copper.



(5) Implication of copper (refining copper).

- Impurities in blister copper = Fe, S, is largely removed by electrolysis to form pure copper.
  - Cathode metal is made anode while the Cu<sup>+</sup> electrode undergoes oxidation to form Copper(II) sulphate solution.
  - \* Copper is deposited at cathode, leaving impurities at the anode.
- Do not write in this margin



### Reactions

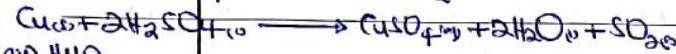
- \* No reaction with water or steam but reacts with molten air forming basic copper(II) carbonate.
- $\text{CuCO}_3 \cdot \text{Cu(OH)}_2 \cdot \text{H}_2\text{O}$
- \* Reacts with oxygen on heating to form copper oxides
- $2\text{CuO} + \text{O}_2 \rightarrow 2\text{Cu}_2\text{O}$
- $4\text{CuO} + \text{O}_2 \rightarrow 2\text{Cu}_2\text{O}_2$
- \* Reacts with halogen on heating to form copper(IV) halides except I<sub>2</sub> which forms copper(II) iodide.
- \* Reactions with acids

(i) No reaction with non oxidising acids (dil HCl, H<sub>2</sub>SO<sub>4</sub>) except in presence of O<sub>2</sub> or oxidising agent

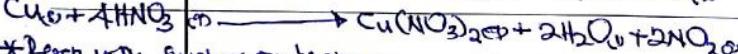
(ii) But conc HCl reacts with copper forming a complex



(iii) Hot conc H<sub>2</sub>SO<sub>4</sub>  $\Rightarrow$  liberates SO<sub>2</sub>



(iv) HNO<sub>3</sub>

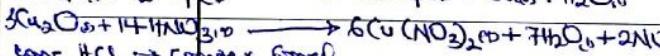


\* Reacts with sulphur on heating.



### Compounds of copper(II)

#### ① Cu<sub>2</sub>O



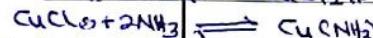
Conc HCl  $\rightarrow$  complex formed



Gases reduced



② CuCl<sub>2</sub> soluble in conc HCl and aqueous ammonia



It dissolves at 1300K & form Cu<sub>2</sub>C<sub>2</sub>.

③ CuI  $\Rightarrow$  black salt precipitated when aqueous soln of copper(II) sulphate u added to aqueous soln of KI



Estimation of % of copper in an ore

\* Known mass of ore is reacted with conc H<sub>2</sub>SO<sub>4</sub> and resultant solution diluted to 250cm<sup>3</sup> in a volumetric flask

\* titrations are carried out in a conical flask and an excess 10% potassium iodide solution added



\* heated volume titrated with standard Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>

using starch indicator



\* Through backward calculation, concentration of copper in 250cm<sup>3</sup> can be calculated. mass of copper can be determined and hence % of copper can be calculated.

$$\% = \frac{\text{mass g} \times 100}{\text{mass g}}$$

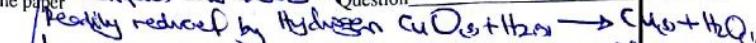
### Copper (II) compounds

$\text{Cu}(\text{H}_2\text{O})_6^{2+}$  ion = Blue in aqueous solution

Acidic due to hydrolysis



Decomposes at acidic & basic Question



Typical basic oxides  $\rightarrow \text{CuO}_{\text{ep}} + 2\text{H}^{\text{ep}} \rightarrow \text{Cu}^{2+} + \text{H}_2\text{O}$



Changes in aqueous ammonia to form deep blue salt



Readily reacts with acids  $\text{Cu}(\text{OH})_{2\text{ep}} + 2\text{H}^{\text{ep}} \rightarrow (\text{Cu}^{2+} + 2\text{H}_2\text{O}$

Decomposes in heat  $\text{Cu}(\text{OH})_{2\text{ep}} \rightarrow \text{CuO}_{\text{ep}} + \text{H}_2\text{O}$

③ CuCl<sub>2</sub>  $\Rightarrow$  dissolves in conc HCl to form a blue

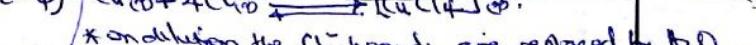
Yellow solution which on dilution turns green blue and finally pale blue.

\* Conc HCl contains large concentration of Cl<sup>-</sup> ions which react with CuCl<sub>2</sub> forming yellow tetrachlorocuprate ion



\* On dilution the Cl<sup>-</sup> ions are replaced by H<sub>2</sub>O

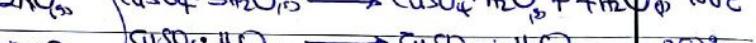
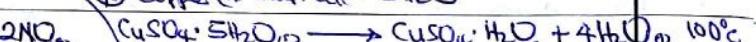
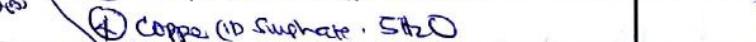
Ligand to form hexaqua cuprate(II) ions where the



NB: Copper(II) white doesn't exist because I<sub>2</sub> is not a powerful oxidising agent to oxidise copper(II) to copper(IV)

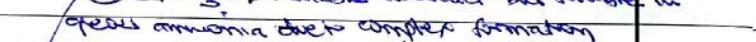
Any attempt yields copper(II) white.

#### ④ Copper(II) Sulphate · 5H<sub>2</sub>O



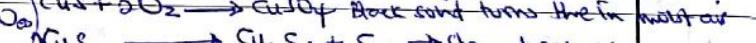
⑤ CuCO<sub>3</sub>  $\Rightarrow$  insoluble in water but soluble in

aqueous ammonia due to complex formation

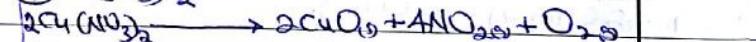


⑥ Cu<sub>2</sub>S  $\Rightarrow$  Black solid; Cu<sup>2+</sup> + S<sup>2-</sup>  $\rightarrow$  Cu<sub>2</sub>S

Cu<sup>2+</sup> + 2O<sub>2</sub>  $\rightarrow$  Cu<sub>2</sub>O<sub>2</sub> Black solid turns the in moist air

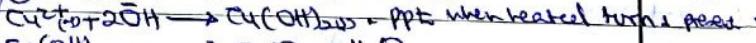


#### ⑦ Cu(NH<sub>3</sub>)<sub>2</sub>

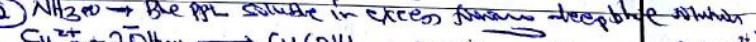


### Aqueous chemistry of copper(II) ions

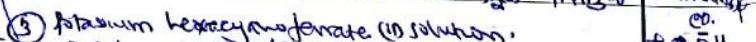
① NaOH  $\Rightarrow$  Blue ppt insoluble in excess



Ppt when heated turns grey



② NH<sub>3</sub>  $\Rightarrow$  Blue ppt soluble in excess ammonia



Blue ppt Brown ppt soluble in ammonia solution

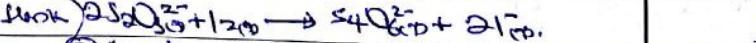
③ Potassium hexacyanoferrate(II) solution



+ Blue ppt Brown ppt soluble in ammonia solution

④ Potassium iodide solution

White ppt Stained brown when long white on addition sodium thiosulphate



⑤ Ammonium thiocyanate solution = Green solution

Ammonium sulphide or H<sub>2</sub>S  $\Rightarrow$  Black solid



⑥ Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>  $\Rightarrow$  Green Ppt



Green Ppt turns yellow when on

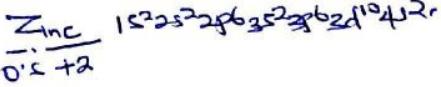


yellow

SEMESTER 2 - 2014/2015 dilution turns blue again



blue



O's +2

Reactions

① Reaction with O<sub>2</sub> on heating



②  $\text{H}_2\text{O} \rightarrow$  N reaction with cold water but reacts with steam to form  $\text{ZnO}$



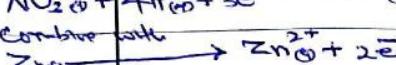
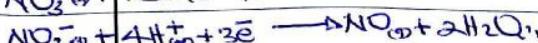
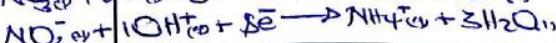
③ Acid

\* Dilute non oxidising acids (dilute HCl,  $\text{H}_2\text{SO}_4$ )

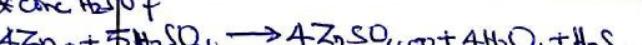


\* Conc  $\text{H}_2\text{SO}_4$   $\text{Zn}(s) + 2\text{H}^+(\text{aq}) \rightarrow \text{ZnSO}_4(\text{aq}) + 2\text{H}_2\text{O}(l) + \text{SO}_2(g)$

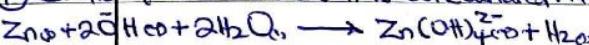
\* Nitric acid  $\Rightarrow$  Product depends on concentration and temperature.



\* Conc  $\text{H}_2\text{SO}_4$  f



④ caustic aqueous alkali & hot concentrated  $\text{NaOH}$ .



⑤ Reaction with salt solution.

$\rightarrow$  fairly strongly electropositive.



⑥ Non-metals  $\Rightarrow$  React on heating



Compounds of Zinc

\* O's +2, appears with  $\text{Zn}(\text{H}_2\text{O})_2^{2+}$

Not ionic because

+ zinc atom has a full 3d orbital.

$\rightarrow$  Has only +2 o's with fully filled 3d orbital.

$\rightarrow$  Compounds are white or colourless since 3d orbital full

+ Not paramagnetic since all 3d electrons paired.

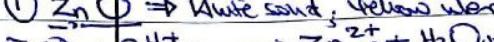
Transition properties

\* forms several complexes with coordination No's of

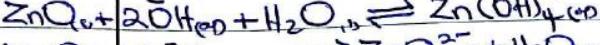
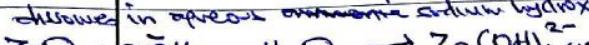
and tetrahedral e.g.  $\text{Zn}(\text{OH})_4^{2-}$ ;  $\text{Zn}(\text{H}_2\text{O})_4^{2-}$ ;  $\text{Zn}(\text{CN})_4^{2-}$

$\text{Zn}(\text{NH}_3)_4^{2+}$ ;  $\text{ZnCl}_4^{2-}$  etc.

①  $\text{ZnO} \Rightarrow$  White solid; yellow when heated; amphoteric



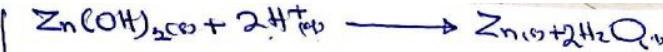
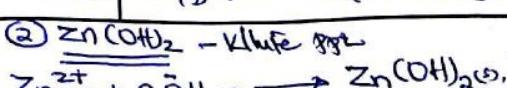
disolves in aqueous ammonia sodium hydroxide



Reduced by C or CO



②  $\text{Zn}(\text{OH})_2$  - White ppt



concentrated alkali  $\Rightarrow$  form Zinate ion.



Question

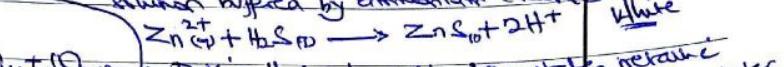
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dissolves in excess ammonia

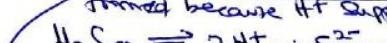


$\text{Zn}(\text{OH})_2$  ppt by ammonia when added with ammonium chloride

③  $\text{ZnS}$  precipitates readily if  $\text{H}_2\text{S}$  passed thru a  $\text{Zn}^{2+}$  solution buffered by ammonium chloride.



\* Passing  $\text{H}_2\text{S}$  into a sulphydrate precipitate remains sulphide but in acidic conditions no precipitate formed because  $\text{H}^+$  suppresses the ionisation of  $\text{H}_2\text{S}$ .



\* This lowers the  $[\text{S}^{2-}]$  ion in solution; only sulphides with low K<sub>sp</sub> can be precipitated e.g.  $\text{CuS}$  but not  $\text{ZnS}$ .

\* This explains why buffering is necessary to eliminate  $\text{H}^+$  or to shift the ionisation equilibrium to right forming more sulphide.

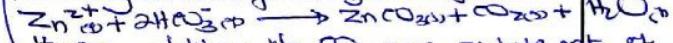
④  $\text{ZnCl}_2$

Heating  $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$  forms anhydrous  $\text{ZnCl}_2$  unlike  $\text{MgCl}_2$  which undergoes hydrolysis in heating.

\* Soluble in organic solvents since it's covalent.

⑤  $\text{ZnCO}_3$   $\Rightarrow$  White sand.

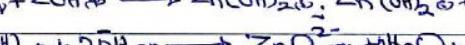
Formed by addition of  $\text{Na}_2\text{CO}_3$  to  $\text{Zn}^{2+}$ .



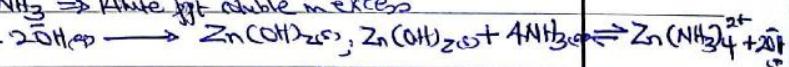
However addition  $\text{Na}_2\text{CO}_3$  gives minute ppt of  $\text{Zn}(\text{OH})_2(s)$  because  $\text{ZnCO}_3$  is more alkaline than  $\text{Na}_2\text{CO}_3$ .

Aqueous chemistry by  $\text{Zn}^{2+}$

① Aqueous  $\text{NaOH} \Rightarrow$  White ppt soluble in excess  $\text{Na}_2\text{CO}_3$  due to  $\text{Zn}(\text{OH})_2(s)$



②  $\text{Ag}^+$   $\text{NH}_3 \Rightarrow$  White ppt soluble in excess



③ Potassium hexacyanoferrate (II) solution.

White ppt soluble in sodium hydroxide



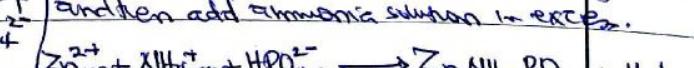
④ Potassium hexacyanoferrate (III) solution.

Yellow ppt insoluble in ammonia



⑤ Addition of disodium hydrogen phosphate.

Add solid  $\text{NH}_4\text{Cl}$ , followed by drops of  $\text{Na}_2\text{HPO}_4$  and then add ammonia solution in excess.



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